

SYNTHESIS OF PYROMELLITIC ACID ESTERS

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(NASA-TM-77977) SYNTHESIS OF PYROMELLITIC  
ACID ESTERS (National Aeronautics and Space  
Administration) 6 p HC A02/MF A01 CSCL 07C

N86-21583

Unclas

G3/23 05711

Translation of "sintez efirov piromellitovoy kisloty," Visnik  
l'vovskogo politekhnicheskogo institut (Journal of the L'vov  
Polytechnic Institute), Vol. 139, 1980, pp. 31-33 (ISSN  
0460-0436) (UDC 547.585.26)



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
WASHINGTON, D.C. 20546 DECEMBER 1985

1. Report No. NASA TM-77977		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle SYNTHESIS OF PYROMELLITIC ACID ESTERS				5. Report Date December 1985	
				6. Performing Organization Code	
7. Author(s) V. A. Fedorova et al.				8. Performing Organization Report No.	
				10. Work Unit No.	
9. Performing Organization Name and Address The Corporate Word, Inc. 1102 Arrott Bldg. Pittsburgh, PA 15222				11. Contract or Grant No. NASW-4006	
				13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautic and Space Administration Washington, DC 20546				14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "sintez efirov piromellitovoy kisloty," Visnik l'vovskogo politekhnicheskogo institut (Journal of the L'vov Polytechnic Institute), Vol. 139, 1980, pp. 31-33 (ISSN 0460-0436) (UDC 547.585.26).					
16. Abstract This article studies the ester acids necessary for studying the thermo- chemical properties of pyromellitic acid (PMK)-based peroxides. It covers obtaining a tetramethyl ester of a PMK. The mechanism of an esterification reaction is discussed, as is the complete esterification of PMK with primary alcohol.					
17. Key Words (Selected by Author(s))			18. Distribution Statement  Unlimited		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 6	22. Price		

## SYNTHESIS OF PYROMELLITIC ACID ESTERS

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When studying the thermochemical properties of pyro- /31\*  
mellitic acid (PMK)-based peroxides, it was necessary to obtain  
complete and n-alkyl ester acids for this acid.

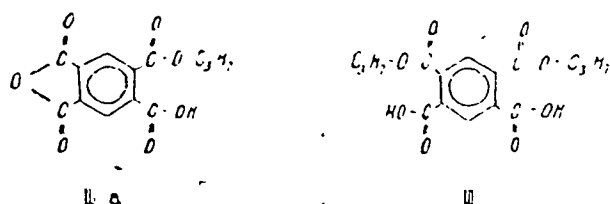
A tetramethyl ester of a PMK is obtained by acylation of  
alcohols PMK in an air-fluidized bed in the presence of special  
catalysts [2], in a liquid phase--in the presence of a  
concentrated sulphuric acid [1] during the interaction of  
pyromellitic dianhydride (PMDA) with dimethyl sulphite at  
110-120°C [3].

The mechanism of an esterification reaction, as it is known,  
corresponds to the following arrangement: primary protonization  
of a carboxylic acid for the formation of active particles of  
electrophilic nature which combines the nucleophilic alcohol with  
the formation of a secondary oxonium ion. This induces the  
migration of a proton from alkylated oxygen to hydroxyl with the  
splitting of a water molecule and the formation of a complex  
ester. The reactivity of anhydrides is higher than that of  
carboxylic acids; therefore, the reaction of esterification  
proceeds with a quantitative yield without the protonization of  
an anhydride, usually in an excess of alcohol. According to  
acylating activities, even the acetic anhydride exceeds PMDA.  
Therefore, the acids of methyl and ether esters were obtained by  
acylation of suitable alcohols for PMK in a multiple excess of  
alcohol (usually 20 moles of alcohol for one mole of PMDA) for  
homogenizing the reaction medium and for completeness of the

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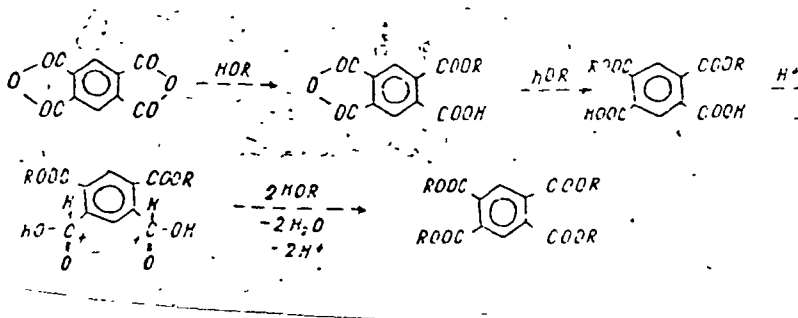
\*Numbers in the margin indicate pagination in the foreign text.

acylation reaction at the boiling temperature of a reaction mass. I and II with a yield of 97.8 and 96.7%, respectively, are obtained by using these methods. The acylation reaction rate of n-propyl alcohol is noticeably decreased as a result of the decrease of its nucleophile; therefore, there is a difference in the activity of two reaction centers of PMDA in relation to n-propyl alcohol. For this reason, after an hour's contact with the reagents, a product of half-esterification of IIIa (80%) is obtained and only 20% of an acidic di-n-propyl ester of PMK (III) is as follows



Further esterification of IIIa was reached by an addition to /32 the reaction mass of catalytic quantities of pyridine.

Complete esterification of PMK with primary alcohol prior to the tetraalkyl esters occurs when the reagents are dissolved in concentrated sulphuric acid. The mechanism of this reaction includes two stages: the formation of acids of dialkyl esters of PMK and then the protonization of carboxyl groups which appeared with a nucleophilic substitution for alkoxy groups according to the arrangement



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In proportion to the increase of a hydrocarbon radical, a steric hindrance occurs in the alcohol, the reaction rate is reduced, and the product yield is decreased. Thus, IV is obtained by this method with a yield of (97.2%), V--94.4%, and VI--91.7%.

Products I--III are crystallized out by diluting the reaction mass with a 5% solution of HCl. These products (I-III) were purified by recrystallizations from suitable water alcohols and then dried in a vacuum. Tetraalkyl pyromellitic IV-VI were crystallized out when the reaction mass was diluted with ten units of cold water. The precipitated crystals were filtered out and purified by the recrystallizations of water alcohols. Synthesized esters were identified by the boiling temperature or by the melting and element analysis (see table).

Characteristics of di- and tetraalkyl pyromellitic esters

Esters	T°, C	Reaction time, hours	Yield %	Melting temp. (Boiling temp.), °C	Found		Formula	Calculated	
					C, %	K. ch.* mg KOH/g		C, %	K. ch.* mg KOH/g
Dimethyl pyromellitic (I)	66	0,5	97,8	27	51,04	398,0	$C_{12}H_{10}O_8$	51,07	397,6
Diethyl pyromellitic (II)	80	0,5	96,7	219	54,22	361,2	$C_{16}H_{14}O_8$	54,19	361,6
Dipropyl pyromellitic (III)	98	0,5	92,4	142	56,71	333,7	$C_{18}H_{16}O_8$	56,79	334,1
Tetramethyl pyromellitic (IV)	108	2,0	97,2	141	54,12	-	$C_{16}H_{14}O_8$	54,19	-
Tetraethyl pyromellitic (V)	122	2,0	94,4	56	58,98	-	$C_{20}H_{18}O_8$	59,01	-
Tetrapropyl pyromellitic (VI)	150	2,0	91,7(242/0,65 millimeters of mercury column)		62,53	-	$C_{24}H_{20}O_8$	62,53	-

\*Translator's note: K. ch. may be Curie unit.

It is apparent from the table that by increasing the hydrocarbon radical of an alkoxyl component, a decrease in the melting temperature associated with the increase in the volume of a molecule takes place. Acid esters have a higher melting temperature and are more easily crystallized than tetraalkyl pyromellitic esters.

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The article was received by the editorial staff on May 16, 1979.